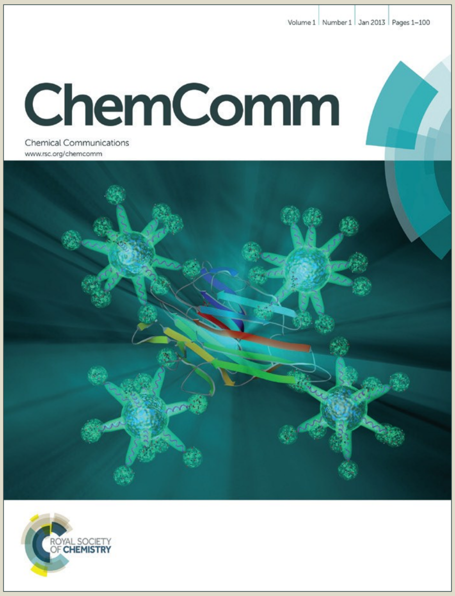
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
ChemComm
Chemical Communications
www.rsc.org/chemcomm
ROYAL SOCIETY OF CHEMISTRY

ChemComm RSCPublishing

COMMUNICATION

A Ruthenium Complex as a Single-Component Redox Shuttle for Electrochemical Photovoltaics

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jeung Yoon Kim,[a] Won Seok Yun,[a] Ho-Jin Son,[b] JaeDong Lee[a] and Nak Cheon Jeong*[a]

A primitive version of ruthenium complex [$Ru(bpy)_3^{2+}$] was employed for the first time as a new conceptual "single-component redox shuttle" for dye-sensitized solar cells. This single shuttle led to a large enhancement of the open-circuit photovoltage (V_{OC}) to ~940 mV relative to that of conventional iodine-based shuttle and greatly increased the efficiency of solar-to-electric energy conversion at lower illumination levels by a factor of *ca.* 5.6.

Inorganic ruthenium complexes have been intensively studied due partly to academic curiosity about their electrochemical natures[1-5] and partly to their possible uses as photoelectron sources in photocatalysis[6-10] and photovoltaics.[11-19] These complexes could possibly have been utilized for dye-sensitized solar cells (DSCs), which are electrochemical photovoltaic devices that are mainly composed of nanoporous semiconductors, chromophores, and redox shuttles. In fact, various ruthenium complexes have been examined as light harvesters in DSCs.[12] These DSCs have exhibited comparable or better solar-to-electric power conversion efficiency (PCE) than high-tech silicon-based solar cells and thus have shown considerable promise as alternatives to these silicon-based technologies. For instance, N719, a ruthenium-based inorganic complex chromophore, has exhibited a PCE greater than 11%.[13]

The major role of a redox shuttle is to reduce and thereby regenerate the oxidized chromophores by delivering electrons from the counter electrode. Another important role of the shuttle is its contribution to generating open-circuit photovoltage (V_{OC}), which is a main factor for gauging the PCE. For more than two dozen years, the room for the shuttle has been thought to be "reserved" by the iodine/iodide couple. Recently, researchers have begun searching for new redox shuttles to attain higher photovoltages, thereby enhancing the PCE. As a result, several shuttles such as cobalt-,[20-26] iron-,[21,27-29] copper-,[21,22,30,31] nickel-,[32] sulfide-,[33-35] and thiocyanate-based shuttles[36] have been discovered. Obviously, these shuttles have enhanced the photovoltage. A cobalt-based shuttle, in particular, resulted in the development of state-of-art DSCs with a PCE greater than 12%.[20] Nevertheless, all the shuttles, whether serendipitously discovered or rationally designed, are commonly "paired form" that is formed by coupling of reduced and oxidized components. For example, iodide (reduced form) in iodine/iodide shuttle is coupled with triiodide, the oxidized form of iodide. Here, we report a new "single-component redox shuttle" that consists of a primitive version of ruthenium complex: tris(2,2'-bipyridyl) ruthenium(II) [$Ru(bpy)_3^{2+}$]. This complex is a counter part of the oxidized form, $Ru(bpy)_3^{3+}$, as a half component of a complete set of the shuttle. The $Ru(bpy)_3^{3+}$ can be readily produced from $Ru(bpy)_3^{2+}$ using strong oxidants such as $NOBF_4$,[37] but it has proven difficult to treat it in ambient condition due to its rapid reduction to $Ru(bpy)_3^{2+}$ (See Supporting Information, Section S1 and S2).[38-44] Also, we have observed that addition of $Ru(bpy)_3^{3+}$ into the $Ru(bpy)_3^{2+}$ electrolyte led to a substantial decrease in both short-circuit photocurrent density (J_{SC}) and open-circuit photovoltage (V_{OC}) (See Supporting Information, Section S3). As described below, however, we find that,

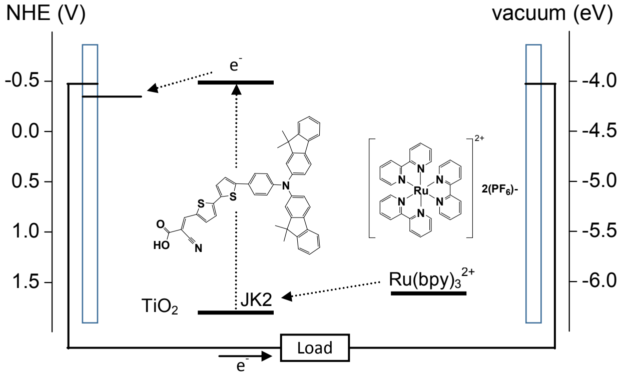

Fig. 1 Schematic energy diagram and structural formulas of the $Ru(bpy)_3^{2+}$ redox shuttle and JK2 dye studied in this work.

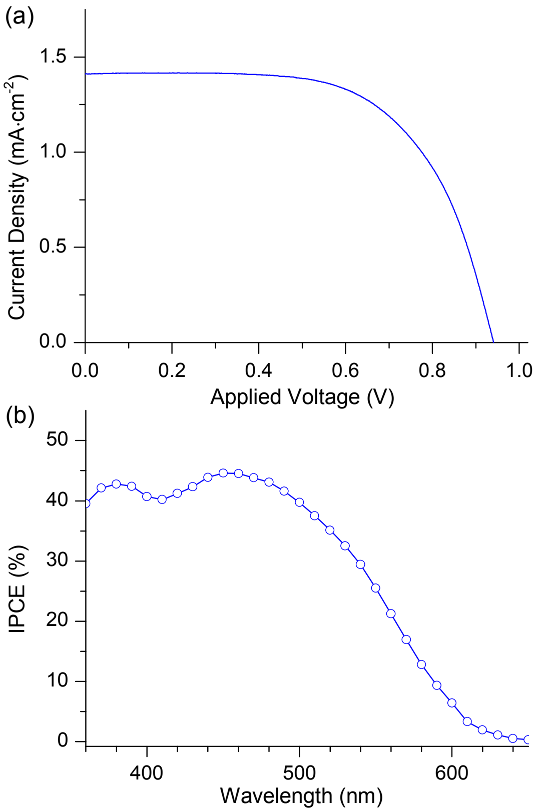

Fig. 2 (a) JV curve and (b) IPCE spectrum of a cell consisting of a 2.4-μm-thick TiO_2 electrode and 8 mM $Ru(bpy)_3^{2+}$ electrolyte.

although it operates solely without its oxidized pair, this new single shuttle performs high open-circuit voltage (*ca.* 950 mV). Notably, this single shuttle boosts the conversion efficiencies under lower power illumination level (i.e., 10 mW·cm^{-2}) by a factor of *ca.* 5.6. More interesting is that ruthenium complexes, to the best of our knowledge, have been rarely considered for use as redox shuttles even though they have been broadly investigated for use in DSCs.[37,45]

One unique feature of ruthenium complexes is their "self-exchange" of electrons. Meyer and colleagues revealed that $Ru(bpy)_3^{2+}$ complexes intermolecularly exchange their electrons (outer-sphere electron-transfer) even in the solution phase.[1] On the basis of this fact, we tested a ruthenium complex to utilize it as a "single-component redox shuttle." The electrolyte solution was simply prepared by dissolving $Ru(bpy)_3{\cdot}2PF_6$ and 4-*tert*-butylpyridine (TBP) in acetonitrile (Supporting Information, Section S1). Essentially, for a DSC to properly function, the redox potential of a shuttle should be higher than the potential of the highest occupied molecular orbital (HOMO) of a chromophore. To determine the redox potential of $Ru(bpy)_3^{2+}$ and to eventually find a suitable chromophore that is compatible with this ruthenium shuttle, we employed cyclic voltammetry and simulated the electronic structure of $Ru(bpy)_3^{2+}$ using density functional theory (DFT) calculations (see the results in Supporting Information, Sections S4 and S5). The resulting redox potential of the ruthenium complex agreed well with the value reported in the literature.[46] Given the aforementioned results, we chose JK2 dye because its quasi-HOMO potential is lower than that of the $Ru(bpy)_3^{2+}$ shuttle (Fig. 1 and Supporting Information, Section S4). With this combination, we optimized the cell performance by varying the thickness of the TiO_2 photoelectrode and the concentration of the $Ru(bpy)_3^{2+}$ electrolyte.

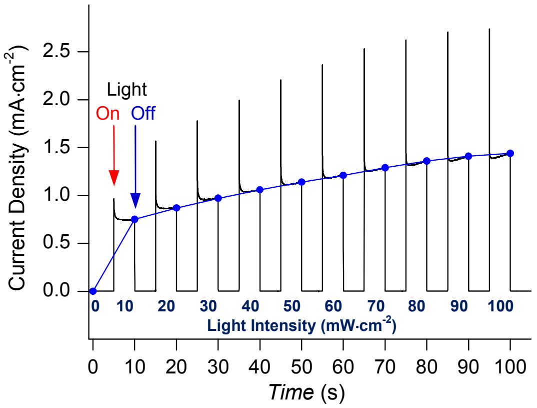

Fig. 3 Chronoamperometric curve showing changes in current density with respect to changes in the illumination power from 0 to 100 mW·cm^{-2} at intervals of 10 mW·cm^{-2}.

Using cells composed of a 2.4-μm-thick TiO_2 film and 8 mM (maximum concentration) $Ru(bpy)_3^{2+}$ electrolyte, we obtained a V_{OC} of 940 mV and a J_{SC} of 1.41 mA·cm^{-2} (see Fig. 2 and Supporting Information, Section S7 and S8).

Obviously, the ruthenium shuttle significantly enhanced the V_{OC} (note that typical iodine/iodide cells exhibit V_{OC} values of *ca.* 700 mV).[14] We attributed this enhancement to the substantially lower oxidation potential of the ruthenium complex {*ca.* 1.58 V vs. the normal hydrogen electrode (NHE); compare this value to the oxidation potential of I^-/I_3^-, which is 0.35-0.93 V}.[15] The J_{SC} values, however, were quite low compared to those of typical I^-/I_3^- cells. We hypothesized that the slow dye-regeneration led to this low current generation. (We note that the "dye-regeneration" here means expansive all processes for reduction of oxidized dye, i.e., electron-transfer from $Ru(bpy)_3^{2+}$ to oxidized dye, mass-transfer of both $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$–the latter is initially absent but transiently formed after donating electron to oxidized dye, and regeneration of $Ru(bpy)_3^{2+}$ from $Ru(bpy)_3^{3+}$ at counter electrode) To confirm this hypothesis, we examined three factors that can influence the dye-regeneration: (i) the electrolyte concentration, (ii) the distance between the dye (in the photoanode) and the counter electrode, and (iii) the intrinsic mass-transfer rate. (We note that, in particular, the latter two factors are mainly governed by transiently formed $Ru(bpy)_3^{3+}$.) First, as previously discussed, we observed that a higher electrolyte concentration resulted in higher current generation (see Section S7 of the Supporting Information). However, we also noted that 8 mM was the maximum concentration of the ruthenium complex in acetonitrile. Second, we intentionally designed cells in which the cross-sectional electrolyte gap interval was rationally modulated from 25 to 175 μm (see Supporting Information, Section S9). As expected, the J_{SC}s decreased as the interval increased. Given that the typical I^-/I_3^- cells did not exhibit this pattern (see Supporting Information, Section S10), we tentatively ascribed this current decrease to slow dye-regeneration resulting from a longer delivery distance. Lastly, smaller nanopores in the TiO_2 electrode can conceivably lead to slower mass-transfer rates relative to larger nanopores. To corroborate this hypothesis, we synthesized smaller TiO_2 nanoparticles (with an average size of *ca.* 10 nm) and used them to fabricate electrodes (see Supporting Information, Sections S1 and S11).[16] As also expected, the smaller pores afforded a lower current density compared to that afforded by larger pores. Accordingly, we reasoned that the low photocurrent output was due to the overall slow dye-regeneration process of this ruthenium electrolyte. In addition, we speculate that transiently formed $Ru(bpy)_3^{3+}$ can also limit current density due to its slow

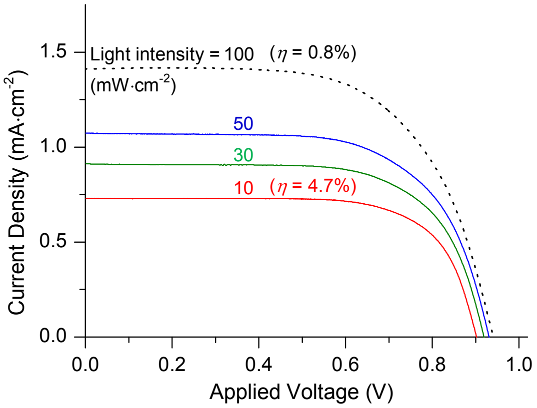

Fig. 4 JV curves of a cell measured under illumination powers of 10 (red), 30 (green), 50 (blue), and 100 (black dots) mW·cm^{-2}.

diffusion to counter electrode.[47-49]

Meanwhile, we consistently observed sizable peak currents when turning on the illuminating light (AM 1.5-simulated one Sun). See Fig. 3. These observations indicates that the instantaneous peak current is always over a critical current saturation point and that the continuous current has already reached its attainable maximum under the simulated 1 Sun. We assumed that this current saturation is attributable to the limited electron-delivery capacity of 8 mM $Ru(bpy)_3^{2+}$ and transiently formed minuscule $Ru(bpy)_3^{3+}$, which can limit dye regeneration.[48,49] To confirm this assumption, an experiment was designed to determine the critical (lowest) light power that could induce current saturation because the number of instantaneously incident photons is strongly associated with the number of instantaneously oxidized dye molecules that lose photoelectrons upon injection but are not yet regenerated by the shuttles, and the number of instantaneously injected photoelectrons is closely correlated with the peak current. The determination of the critical light power was achieved by testing chronoamperometric current changes upon the power of the illuminating light from 0 (dark) to 100 mW·cm^{-2} (Fig. 3). While the peak current was substantially reduced as the illumination intensity was decreased, the reduction of the continuous current was not as significant. For instance, even though the illumination power was decreased by a factor of 10, the continuous current density at 10 mW·cm^{-2} (0.75 mA·cm^{-2}) was only half that at 100 mW·cm^{-2} (1.44 mA·cm^{-2}). Also, the magnitude of the peak current at 10 mW·cm^{-2} (0.22 mA·cm^{-2}) was substantially low relative to those over the other illumination ranges (0.72-1.35 mA·cm^{-2}). In view of these results, we speculated that the critical illumination power for continuous dye regeneration is similar to or less than 10 mW·cm^{-2} (0.1 Sun).

These experiments suggested that the ruthenium electrolyte would likely exhibit better PCE performance under low-power illumination. With this assumption in mind, we examined the applied voltage-to-current output (JV) responses to several illumination powers (see Fig. 4 and Table 1). The cell exhibited J_{SC} values of 1.41, 1.07, 0.91, and 0.73 mA·cm^{-2} under illumination powers of 100, 50, 30, and 10 mW·cm^{-2}, respectively. These results showed that, in contrast to the steep decrease in the illumination power, the decrease in the J_{SC} was relatively gradual. Thus, the PCE at 10 mW·cm^{-2} (*ca.* 4.7%), by contrast, was enhanced by 5.6-fold with a reduction in the light power (compared with a PCE of *ca.* 0.8% at 100 mW·cm^{-2}). Interestingly, such a dramatic enhancement of PCE corresponding to changes in the illumination power has been rarely reported.[20,50-52] Given that the PCE at 10 mW·cm^{-2} (*ca.* 4.7%) is comparable to that of typical I^-/I_3^- cells (*ca.* 5.1%) although the concentration of $Ru(bpy)_3^{2+}$ (8 mM) is *ca.* 90-fold less than that of I^- (700 mM), we expect that the use of the ruthenium electrolyte would likely be highly cost-efficient (see the Supporting Information, Section S12).

Table 1 Photovoltaic Parameters Measured under Illumination Powers of 10, 30, 50, and 100 mW·cm^{-2}

Light Power (mW·cm^{-2})	J_{SC} (mA·cm^{-2})	V_{OC} (V)	*FF*	η (%)
10	0.73	0.90	0.71	4.67
30	0.91	0.92	0.68	1.90
50	1.07	0.93	0.64	1.27
100	1.41	0.94	0.63	0.83

In summary, a new conceptual single-component redox shuttle, $Ru(bpy)_3^{2+}$, led to a large enhancement in V_{OC} (~940 mV) relative to the V_{OC} of cells containing the standard iodine-based shuttle. The enhanced V_{OC} was ascribed to the relatively low oxidation potential of the ruthenium complex. Furthermore, this shuttle greatly boosted PCE under low-power illumination conditions by approximately six-fold, suggesting that this shuttle is suitable for indoor use. Although the photocurrent output was quite low in this beginning step, chemical modification to the ruthenium complex to increase its concentration is expected to eventually magnify both the J_{SC} and the PCE. We also anticipate that this ruthenium shuttle can be applied as an alternative electrolyte for quantum-dot solar cells (QDSCs) because of its low corrosiveness. This new concept should also be transferable to other solar cells, such as those with solid-state molecular electrolytes.

This work was supported by the Ministry of Science, ICT, and Future Planning (MSIP) of Korea, under the auspices of the Basic Science Research Program sponsored by the National Research Foundation (NRF) (Grant No.: NRF-2013R1A1A1010254) and by the DGIST R&D Program (Grant No.: 13-BD-0403). J.L. also acknowledges support from MSIP via the Basic Science Research Program sponsored by the NRF (Grant No.: NRF-2013R1A1A2007388).

Notes and references

[a] Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711-873, Korea. *E-mail: nc@dgist.ac.kr*

[b] Department of Advanced Materials Chemistry, Korea University, Sejong 339-770, Korea

† Electronic Supplementary Information (ESI) available: Experimental details, Photograph images, CV data, UV-vis absorption spectrum, J-V characteristics, IPCE spectra, SEM images, and TEM images. See DOI: 10.1039/c000000x/

1 R. C. Young, F. R. Keene and T. J. Meyer, *J. Am. Chem. Soc.*, 1977, **99**, 2468-2473.

2 M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003-3036.

3 K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159-244.

4 C. Creutz and N. Sutin, *Inorg. Chem.*, 1976, **15**, 496-499.

5 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem.*, 1983, **22**, 1617-1622.

6 J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. M. Iha, J. L. Templeton and T. J. Meyer, *Acc. Chem. Res.*, 2009, **42**, 1954-1965.

7 M. D. Doherty, D. C. Grills, J. T. Muckerman, D. E. Polyansky and E. Fujita, *Coord. Chem. Rev.*, 2010, **254**, 2472-2482.

8 M. Gratzel, *Nature*, 2001, **414**, 338-344.

9 W. J. Youngblood, S. H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust and T. E. Mallouk, *J. Am. Chem. Soc.*, 2009, **131**, 926-927.

10 W. J. Song, A. Ito, R. A. Binstead, K. Hanson, H. L. Luo, M. K. Brennaman, J. J. Concepcion and T. J. Meyer, *J. Am. Chem. Soc.*, 2013, **135**, 11587-11594.

11 J. Desilvestro, M. Gratzel, L. Kavan, J. Moser and J. Augustynski, *J. Am. Chem. Soc.*, 1985, **107**, 2988-2990.

12 B. Oregan and M. Gratzel, *Nature*, 1991, **353**, 737-740.

13 M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho and M. Gratzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835-16847.

14 N. C. Jeong, H. J. Son, C. Prasittichai, C. Y. Lee, R. A. Jensen, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 19820-19827.

15 G. Boschloo and A. Hagfeldt, *Acc. Chem. Res.*, 2009, **42**, 1819-1826.

16 N. C. Jeong, O. K. Farha and J. T. Hupp, *Langmuir*, 2011, **27**, 1996-1999.

17 J. N. Clifford, E. Martinez-Ferrero, A. Viterisi and E. Palomares, *Chem. Soc. Rev.*, 2011, **40**, 1635-1646.

18 G. J. Meyer, *ACS Nano*, 2010, **4**, 4337-4343.

19 T. Kinoshita, J. T. Dy, S. Uchida, T. Kubo and H. Segawa, *Nat. Photonics*, 2013, **7**, 535-539.

20 A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Gratzel, *Science*, 2011, **334**, 629-634.

21 T. Stergiopoulos and P. Falaras, *Adv. Energy Mater.*, 2012, **2**, 616-627.

22 S. Yanagida, Y. H. Yu and K. Manseki, *Acc. Chem. Res.*, 2009, **42**, 1827-1838.

23 C. A. Bignozzi, R. Argazzi, R. Boaretto, E. Busatto, S. Carli, F. Ronconi and S. Caramori, *Coord. Chem. Rev.*, 2013, **257**, 1472-1492.

24 S. A. Sapp, C. M. Elliott, C. Contado, S. Caramori and C. A. Bignozzi, *J. Am. Chem. Soc.*, 2002, **124**, 11215-11222.

25 J. H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J. E. Moser, C. Y. Yi, M. K. Nazeeruddin and M. Gratzel, *Nat. Commun.*, 2012, **3**, Article Number 631.

26 E. Mosconi, J. H. Yum, F. Kessler, C. J. G. Garcia, C. Zuccaccia, A. Cinti, M. K. Nazeeruddin, M. Gratzel and F. De Angelis, *J. Am. Chem. Soc.*, 2012, **134**, 19438-19453.

27 T. Daeneke, T. H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach and L. Spiccia, *Nat. Chem.*, 2011, **3**, 211-215.

28 T. Daeneke, Y. Uemura, N. W. Duffy, A. J. Mozer, N. Koumura, U. Bach and L. Spiccia, *Adv. Mater.*, 2012, **24**, 1222-1225.

29 T. W. Hamann, O. K. Farha and J. T. Hupp, *J. Phys. Chem. C*, 2008, **112**, 19756-19764.

30 S. Hattori, Y. Wada, S. Yanagida and S. Fukuzumi, *J. Am. Chem. Soc.*, 2005, **127**, 9648-9654.

31 Y. Bai, Q. J. Yu, N. Cai, Y. H. Wang, M. Zhang and P. Wang, *Chem. Commun.*, 2011, **47**, 4376-4378.

32 T. C. Li, A. M. Spokoyny, C. X. She, O. K. Farha, C. A. Mirkin, T. J. Marks and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 4580-4582.

33 M. K. Wang, N. Chamberland, L. Breau, J. E. Moser, R. Humphry-Baker, B. Marsan, S. M. Zakeeruddin and M. Gratzel, *Nat. Chem.*, 2010, **2**, 385-389.

34 L. F. Liu, X. Li, J. Z. Chen, Y. G. Rong, Z. L. Ku and H. W. Han, *Sci. Rep.*, 2013, **3**, Article Number 2413.

35 A. Hilmi, T. A. Shoker and T. H. Ghaddar, *ACS Appl. Mater. Interfaces*, 2014, **6**, 8744-8753.

36 P. Wang, S. M. Zakeeruddin, J. E. Moser, R. Humphry-Baker and M. Gratzel, *J. Am. Chem. Soc.*, 2004, **126**, 7164-7165.

37 J. W. Ondersma and T. W. Hamann, *J. Am. Chem. Soc.*, 2011, **133**, 8264-8271.

38 E. A. Seddon and K. R. Seddon, in *The Chemistry of Ruthenium,* Elsevier Science Publishers B. V., New York, 1984, p 269.

39 M. Trojanowicz, in *Advances in Flow Analysis,* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008, p 616.

40 R. E. Desimone and R. S. Drago, *J. Am. Chem. Soc.*, 1970, **92**, 2343-2352.

41 M. Biner, H. B. Burgi, A. Ludi and C. Rohr, *J. Am. Chem. Soc.*, 1992, **114**, 5197-5203.

42 K. Matsuura and L. Kevan, *J. Phys. Chem.*, 1996, **100**, 10652-10657.

43 R. D. Gerardi, N. W. Barnett and P. Jones, *Anal. Chim. Acta*, 1999, **388**, 1-10.

44 G. P. McDermott, P. Jones, N. W. Barnett, D. N. Donaldson and P. S. Francis, *Anal. Chem.*, 2011, **83**, 5453-5457.

45 W. D. K. Clark and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 4676-4682.

46 E. Ronca, F. De Angelis and S. Fantacci, *J. Phys. Chem. C*, 2014, **118**, 17067-17078.

47 T. W. Hamann and J. W. Ondersma, *Energy & Environmental Science*, 2011, **4**, 370-381.

48 N. Papageorgiou, M. Gratzel and P. P. Infelta, *Sol. Energy Mater. Sol. Cells*, 1996, **44**, 405-438.

49 J. J. Nelson, T. J. Amick and C. M. Elliott, *J. Phys. Chem. C*, 2008, **112**, 18255-18263.

50 H. J. Snaith, *Adv. Funct. Mater.*, 2010, **20**, 13-19.

51 A. K. Chandiran, A. Yella, M. Stefik, L. P. Heiniger, P. Comte, M. K. Nazeeruddin and M. Gratzel, *ACS Appl. Mater. Interfaces*, 2013, **5**, 3487-3493.

52 H. Nusbaumer, S. M. Zakeeruddin, J. E. Moser and M. Gratzel, *Chem.-Eur. J.*, 2003, **9**, 3756-3763.

Table of Contents

A new conceptual “single-component redox shuttle” led to a large enhancement of V_{OC} (~940 mV) and also greatly boosted the energy conversion efficiency under low-power illumination level by a factor of *ca.* 5.6.